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THE OZONE FORM OF HYDROGEN

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Communicated by W. A. Noyes, September 22, 1919

In spite of its having only a single valence bond, hydrogen seems to form an active variety bearing the same relation to ordinary hydrogen that ozone bears to oxygen. The chemical activity of this form of hydrogen is not attributable to single free atoms, since the characteristics of the atomic form are well known, and different from those of this ozone form.

Professor Sir J. J. Thomson,[1] in working with positive rays in 1912, showed the existence in a hydrogen discharge tube of particles with a molecular weight of 3. He gave the tentative symbol of X_3 to this material, and investigated its chemical properties in some detail. He found that it combines with oxygen under the action of light. It is also destroyed by sparking with oxygen, as well as by being heated in a quartz tube with copper oxide. In the absence of oxygen the gas could be heated to a high temperature without destruction. Attempts to obtain spectroscopic evidence of the new form of hydrogen failed, only the usual spectrum being evident.

An investigation begun in 1914 with the co-operation of Professor William Duane[2] showed that hydrogen becomes chemically active under the influence of alpha rays from radium emanation, and that when this active variety is formed there is a distinct contraction in volume. The active hydrogen attacks sulphur, forming hydrogen sulphide. This reaction is the simplest test for the presence of the active modification: The hydrogen is activated by the rays; it is allowed to pass over sulfur, and then passes over a strip of filter paper moistened with lead acetate which it blackens, due to the hydrogen sulphide present. Other reactions are equally simple and characteristic. It reduces neutral permanganate solution to give a precipitate of manganese dioxide; acid permanganate is entirely decolorized, giving a manganous salt. Arsenic is reduced to arsine; phosphorus gives phosphine. There is some action even on mercury, giving a lustrous yellow compound, presumably a hydride, which decomposes on heating. This activity is not due to the presence of charged molecules or ions, as these can be completely removed by an electrostatic field of a thousand volts per centimeter without destroying the chemical activity of the gas.

The active modification is unstable, and must be allowed to react with the oxidizing substance within three or four minutes of the time of its formation. Here again its properties are those to be expected from an ozone form. Passage of the gas through a tube immersed in liquid air destroys its activity either by condensing the active variety which thus has a boiling point very much higher than that of ordinary hydrogen, or by causing its disintegration into ordinary H_2.

A molecule larger than H_2 is indicated by various facts. The purest obtainable hydrogen contracts when under the influence of alpha rays. This has recently been confirmed by Lind,[3] working with large quantities of radium emanation. Usher,[4] working in Ramsay's Laboratory in 1909, observed the same effect, but attributed the loss of volume to the projection of hydrogen molecules into the glass walls of the retaining vessel when bombarded by alpha rays, although the volume of hydrogen lost was larger than the number of alpha rays would permit, and although he was also unable to regain an adequate volume of hydrogen when the glass walls were pulverized and heated.

The second line of evidence results from Langmuir's[5] preparation of an active form of hydrogen which is probably monoatomic. This hydrogen is present in an electric light bulb when the filament is heated to a high temperature, and is undoubtedly a consequence of the dissociation of hydrogen molecules at the high temperature of the filament. When the pressure in the bulb is very low this atomic form of hydrogen forms a layer on the inner surface of the glass wall, and although thus attached, is chemically active. It reacts rapidly with phosphorus vapor, for instance. It has two marked characteristics which distinguish it from the ozone form; namely, that it will not pass through a plug of glass wool, being adsorbed strongly by this substance; and secondly, that it does not exist except at the very highest vacua. When more hydrogen is admitted into the bulb than is necessary to make a layer one atom deep on the glass wall, the amount of active hydrogen is much reduced, the excess molecules seeming to react with the active atoms. The ozone form of hydrogen, on the other hand, will pass through long layers of glass wool and exists for some time at atmospheric pressure.

The third and direct evidence that this hydrogen is polyatomic is found in the work of Sir J. J. Thomson and of Dempster,[6] both of whom made use of the method of positive ray analysis to determine the constituents of a gaseous mixture in the presence of an electric discharge at high vacuum. The photographic method of Thomson and the electrical measurement method of Dempster both show the presence of considerable quantities of H_3 in an H_2 tube. At pressures of 0.05 mm., indeed, Dempster has shown that H_3 predominates.

Very recent work has shown that this active hydrogen is present in large quantities in any ordinary hydrogen discharge tube. A Geissler tube under a pressure as high as 6 cm. contains the ozone hydrogen. If hydrogen is passed continuously through such a tube and is then allowed to react with sulfur a lead acetate paper is decidedly blackened in the course of two or three minutes. Potassium permanganate is decolorized with equal speed. This is an effective lecture experiment. No ions are present in this hydrogen, as can readily be shown by passing the gas through a sensitive emanation electroscope. When this instrument is sensitive enough to detect 10-12 Curie of radium emanation with ease, the electroscope leaf remains perfectly steady though the active hydrogen is passed through for hours. The activity is therefore due to molecules.

The mechanism by which these larger and unstable molecules are formed is still obscure. In the case of their formation under the action of alpha rays they may be the product of the bombardment of ordinary hydrogen molecules by means of the swift and very energetic alpha particles. A hydrogen atom thus projected by bombardment into an ordinary hydrogen molecule may remain there in the metastable condition of a triatomic molecule. The formation of this variety of hydrogen, however, in the cathode ray discharge tube, where the only bombardment is by a stream of electrons, indicates that probably nothing more than ionization is necessary. The most plausible hypothesis is that the ions collect about them a cluster of molecules, forming a so-called large ion, and that the valence bonds in such a group are so disintegrated that the cluster breaks down with the formation of various types of fragments, among them H_3 as well as H_2. Cluster ions are undoubtedly present in such a tube, though their quantity is hard to estimate. Dempster has shown, however, that at low pressures both H_3 and H_2 are present in large quantities, with H_3 predominating in certain ranges of pressure. Still more information on the mechanism of the formation of this type of molecule would be obtainable from a study of the action of very short wave-length light on hydrogen. The Schumann region of the spectrum is absorbed by hydrogen, and the ionization or molecule shattering that probably then occurs may also give rise to this ozone form. This phase of the question is now being investigated.

The existence of such a molecule as H_3 does not accord with the present theories of valence. The univalence of hydrogen is the basis of the present theory, and no diagram of H_3 can be made without in one manner or another splitting the single unitary valence bonds into fractions, as for instance is possible with the conception of J. Stark. H_3 has been shown to be consistent with Bohr's model of the hydrogen atom. But the chemist will require a more definite picture to show the structure of this compound and to reconcile its very ordinary existence and properties with his theoretical conceptions. Hydrogen seems no different from oxygen in this regard. Indeed, it is probably only the injunction due to the valence theory which has prevented the observation of this variety of hydrogen at a much earlier time than the present.

[1] *Rays of Positive Electricity*, Longmans, 1913.

[2] Duane and Wendt, *Ithaca, Physic. Rev.* **10,** 1917, (116–128).

[3] S. C. Lind, *Easton, Pa., J. Amer. Chem. Soc.*, **41,** 1919, (545).

[4] F. L. Usher, *London, J. Chem. Soc.*, **97,** 1909, (400).

[5] Irving Langmuir, *J. Amer. Chem. Soc.*, **34,** 1912, (860, 1310); **36,** 1914, (1708); **37,** 1915, (417).

[6] A. J. Dempster, *London, Phil. Mag.*, **31,** 1916, (438–43).

A VAPOR-FREE VACUUM SEAL

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Communicated by J. S. Ames

The behavior of stop-cocks in vacuum manipulations is, as a rule, quite satisfactory so long as the degree of exhaustion is not very high. However, when the utmost vacuum must be reached and maintained, the ordinary stop-cock is useless. Quite apart from its tendency either to leak or to fill up with grease, its main defects are: 1. Evaporation of volatile constituents of the grease into the evacuated chamber. 2. Comparatively small diameter of opening. Another element has been brought to light by Shrader who has recently shown (*Physical Review, Ithaca*, June, 1919, p. 434) that the gases liberated from the seal, when a glass bulb is sealed off the pump, increase the pressure several hundred per cent over that which had existed previously. An attempt has been made to overcome these difficulties by designing a vacuum seal of the type shown in sketch.

The apparatus takes the form of the well-known trap, slightly modified. A hollow cylinder of platinum (A), either seamless or made